(54) Title: COMPOSITIONS AND PROCESSES FOR TREATING SUBTERRANEAN FORMATIONS

(57) Abstract: A method and materials for stabilizing a wellbore against excess fluid pressure is described. It comprises forming or placing a flexible and essentially impermeable lining on or in the wellbore wall. The flexibility of the lining ensures that it remains in compression as the pressure in the wellbore is increased above the fluid pressure in the surrounding rock and it therefore does not need high tensile strength. The lining may be a preformed elastomer sleeve or formed in situ by the use of a reactive drilling fluid. Appropriate reactive formulations are described for the situation where the rock contains significant quantities of clay.

WO 01/98627 A1

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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Compositions and processes for treating subterranean formations

This invention relates to compositions and methods for
stabilizing subterranean formations surrounding a borehole. More
5   specifically, it pertains to additives for drilling and remedial
fluids or other materials and methods used to improve the
mechanical properties of the wall of the borehole.

BACKGROUND OF THE INVENTION

10

Drilling operations typically involve mounting a drill bit on
the lower end of a drill pipe or "drill stem" and rotating the
drill bit against the bottom of a hole to penetrate a formation,
creating a borehole. A drilling fluid, typically referred to as
15   "drilling mud", may be circulated down through the drill pipe,
out the drill bit, and back up to the surface through the
annulus between the drill pipe and the borehole wall. The
drilling fluid has a number of purposes, including cooling and
lubricating the bit, carrying the cuttings from the hole to the
20   surface, and exerting a hydrostatic pressure against the
borehole wall to prevent the flow of fluids from the surrounding
formation into the borehole.

A drilling fluid can place undesirable mechanical stress on the
25   rock around the wellbore and may even damage the reservoir. With
increasing depth a hydrostatic pressure acts outward on the
borehole, which may cause mechanical damage to the formation and
reduce the ability of the well to produce oil or gas. Drilling
fluids also may fracture the formation, requiring a drilling
30   shut down in order to seal the fracture. Damage to a reservoir
is particularly harmful if it occurs while drilling through the
"payzone," or the zone believed to hold recoverable oil or gas.

Therefore, after a section of the wellbore has been drilled,
35   drilling operations are stayed or ceased to seal the wellbore

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using a string of pipe such as casing or a liner in the well
bore. The stops are commonly referred to as "casing points". At
a casing point, a sealing composition such as hydraulic cement
slurry is pumped into the annular space between the walls of the
5   well bore and the exterior of the string of pipe disposed
therein. The cement slurry is permitted to set in the annular
space thereby forming an annular sheath of hardened
substantially impermeable cement therein. The cement sheath
physically supports and positions the pipe in the well bore and
10 bonds the pipe to the walls of the well bore whereby the
undesirable migration of fluids between zones or formations
penetrated by the well bore is prevented. This well-established
technique has several disadvantages, including a reduction in
the well diameter after each casing point and the high cost of
15 the casing itself.

Thus, there is a continuing need for improved methods and
sealing compositions for sealing subterranean zones through
which fluids undesirably flow into or out of the wellbores
20 penetrating the zones and for simultaneously increasing the
mechanical strengths of the wellbore.

PRIOR ART

25 In addition to the above-mentioned practice of casing and liner
completion, it is known to consolidate formations with a fluid
containing polymerizable or hardening materials, such as
epoxides, resins or isocyanates in combination with diols. Those
methods are described for example in the United States Patent
30 Nos. 6012524, 5911282, 5242021, 5201612, 4965292, 4761099,
4715746, 4703800, 4137971, or 3941191. In the recent
International Patent Application WO 99/31353 there are described
various compositions to stabilize clay formations through in-
situ polymerization that significantly changes the resistance of
35 the clay to swelling and dispersion on contact with water.

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It is further known to apply rubber and latex based materials for remedial operations, such as United States Patent Nos. 4,649,998 and 5,159,980. These techniques usally assume the existence of drilled wellbore and are applied locally to treat
5 defects in the casing or cement. Or the treatment is applied to weakly consolidated sand formations, i.e. in highly porous formations.

In view of the above, it is an object of the invention to
10 provide a novel method of stabilizing subterranean formations surrounding a borehole, particularly clayey or shale formations.

SUMMARY OF THE INVENTION
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In accordance with the present invention there is provided a flexible lining to the wellbore. The lining material is designed to be more flexible and less permeable than the formation so that when the wellbore pressure exceeds the pore
20 pressure the lining deforms more than the rock and remains in compression. The rock then provides mechanical support to the lining material, which therefore does not need a high (tensile) strength.

25 The desirable property of the lining material is met when its shear modulus G_L is smaller than the shear modulus of the formation rock G_R. It is even more advantageous to have the ratio G_L / G_R limited by the Poisson's ratio v of the lining.

30 In a preferred embodiment, the lining material has a reduced permeability compared with the surrounding formation. Said formation being clayey implies that the lining is essentially impermeable.

35 According to a further preferred aspect of the invention, the

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lining is generated during or shortly after the drilling
process. In other words, it is applied prior to casing and
cementing and may extend the interval between casing points.

5   In a more specific embodiment, the lining material is generated
through a chemical reaction of a precursor material that,
preferably, can be added to the drilling fluid without impairing
its other properties. In another specific embodiment the
material is applied as a foil, preferably through an extrusion
10   process or by pushing a liner from the surface or a combination
of both.

When the fluid pressure in the wellbore exceeds the pressure
that initiates hydraulic fracturing in the unlined formation,
15   fractures will be initiated in the rock but they will be
prevented from propagating by the lining material which stops
fluid from entering the fracture and pressurizing the crack tip.
We also note that the rock may enter plasticity, so the tensile
crack may not even be initiated. The result of applying the
20   lining will be an increase in the apparent fracture pressure of
the rock formation, opening the mud window and allowing a
greater length of well to be drilled before a conventional steel
casing is set.

25   There are two main applications of the invention. Firstly, it is
envisaged that a drilling mud formulation containing a
combination of the specified compounds described below may be
used to maintain the integrity of the wellbore during
conventional drilling operations. Secondly, a fluid formulation
30   containing a combination of the same compounds may be used for
general remedial operations in the wellbore. Finally, the
invention may be used to achieve the goal of "casingless
drilling", that is to achieve with one and the same drilling and
completion fluid the equivalent result of what is today obtained
35   through a combination of drilling, casing and cementing

operations. Or, the invention may reduce the number or casing points required to complete the drilling.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

BRIEF DESCRIPTION OF DRAWINGS

FIG 1.   shows the resulting change in permeability as a reaction in accordance with an example of the present invention progresses through a core sample;

FIG 2.   is a flow chart illustrating major steps of a method in accordance with the present invention.

EXAMPLE(S) FOR CARRYING OUT THE INVENTION

The lining as envisaged by this invention could be either produced continuously during the drilling process or intermittently while drilling is suspended. Both preformed sleeving and material deposited downhole to produce the lining are appropriate. An advantage of the preformed sleeve is that the elastomer material properties can be optimized without the constraints imposed by an in situ production process. However, the lining formed downhole has the advantage of conforming to the shape of the wellbore, which may be irregular.

The solid mechanics of an impermeable liner in a wellbore can be summarized for the case of a thin liner (compared to the radius of the wellbore) by a stress concentration factor K defined as:
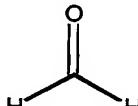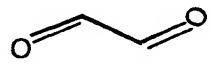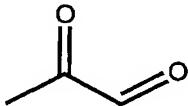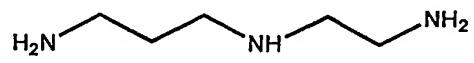
- 6 -
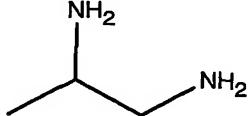
[1] $$K = -\frac{G_1/G_r - \nu}{1 - \nu}$$

where ν is Poisson's ratio for the lining and G_l and G_r are the shear modulus of the lining material and the rock respectively. The lining is in tension if K is negative and the wellbore pressure exceeds the far field pressure. Therefore, the lining will always be in compression when $G_l/G_r < \nu$.
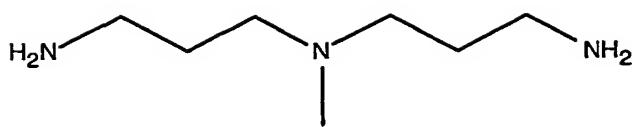
The structures of the chemicals compounds of potential use in the inventive process are shown in Table 1.

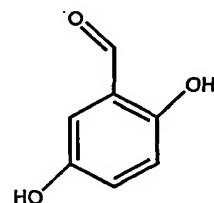Table 1 Structures of Amine Aldehyde Chemicals.

Compound	STRUCTURE
Formaldehyde	
Glyoxal	
Pyruvic Aldehyde	
NAP	
BNH2	$CH_3CH(NH_2)CH_2-[OCH(CH_3)CH_2]_l-[OCH_2CH_2]_m-[OCH_2CH(CH_3)]_n-NH_2$
1,3 DA	
1,2 DA	

3NH2

DHB

Some trends can be discerned in the performance of the different
chemical structures. Considering first the amines, branched
compounds appear to perform better than the linear ones. Thus,
5 1,2 DA and 3NH2 are superior to 1,3DA and NAP respectively.
Additionally, incorporating EO/PO groups as with BNH2, which are
known to adsorb strongly on the clay and inhibit clay swelling,
did not result in impressive permeability reductions. Comparing
the aldehydes, the performance of the three small aldehydes was
10 similar, with pyruvic aldehyde marginally exceeding the others.

The elasticity of the treated shale is a key parameter in the
proposed wellbore lining technique, as the elastic modulus must
be lower than that of the untreated shale for the lining to
15 remain in compression as the pressure in the wellbore increases.

The mechanical properties of films treated with formaldehyde,
glyoxal or pyruvic aldehyde and either 1,2 DA or 3NH2 are shown
in Table 2. The 1,2DA pyruvic aldehyde treatment appears to
20 increase both the tensile strength and the Young's and shear
modulus compared to the untreated film. In all the other cases
the treated films were more elastic than the untreated. Note
that the 3NH2/pyruvic aldehyde has particularly good performance
in that the tensile strength was increased in addition to a
25 significant the reduction in the Young's and shear moduli.

Table 2 Mechanical Properties of Treated and Untreated Clay
Films

Clay Film Treatment	Tensile Stress (MPa)	Young's Modulus (GPa)	Shear Modulus (GPa)
Untreated samples	7.8	2.7	9.1
1,2DA/Glyoxal	12.2	2.2	7.3
1,2DA/Pyruvic Aldehyde	13.8	3.9	13.1
3NH2/Formaldehyde	3.0	0.94	3.1
3NH2/Glyoxal	7.4	2.2	7.3
3NH2/Pyruvic Aldehyde	15.9	2.2	7.2

In further experiments core samples were used to test the mechanical properties of shales modified in accordance with

5   examples of the invention. Shale samples were prepared by cutting 1 inch diameter cores into 2 mm thick slices and polishing one face to a roughness of less than 1μm using diamond paste. The prepared samples were tested in a concentric ring-on-ring jig, which was built for this purpose.

10

Results from this test are shown in Table 3,below. All cores have been drained at 10 MPa and exposed to fluids in a Hassler cell under a confining pressure of 8.0 MPa.

15 The core which has been treated with a BNH2/Glyoxal solution was used in the Hassler Cell experiment in which fluid was pumped through the core for an extended period of time until no further change in permeability occurred (see also FIG. 1 below). The Young's and shear modulus of the treated Oxford Clay were

20 smaller in both cases than those of the untreated (pore fluid only) shale indicating the desired increase in flexibility, in contradiction of the results with the clay films. While the BNH2/Glyoxal did little to the tensile strength of the core while drastically reducing the moduli, the 3NH2 increased the

tensile strength while marginally reducing the moduli compared
to the core which had only seen pore fluid.

Table 1 Mechanical Properties of Treated and Untreated Shales

Shale Sample	Strength (MPa)	Young's Modulus (GPa)	Shear Modulus (GPa)
Pore Fluid Only	5.3	6.51	19.7
BNH2 /Glyoxal	5.2	0.27	0.82
3NH2/Pyruvic Aldehyde	7.9	5.75	17.4

Another aspect of the invention is the desired reduction in
permeability afforded to the formation by the invention.

Experiments using a test cell with a thin clay film membrane
show that the inherently low permeability of shale can be
further reduced by a variety of chemical compositions. Results
of those tests are shown in Table 4.

Table 4 Permeability Reduction in Clay Films Due to
Polymerisation

Chemistry	Permeability Reduced to
Glyoxal/NAP	75%
Glyoxal/BNH2	46%
Glyoxal/1,3DA	55%
Glyoxal/3NH2	42%
Glyoxal/1,2DA	19%
Formaldehyde/BNH2	66%
Formaldehyde/3NH2	15%
Pyruvic Aldehyde/3NH2	10%

Pyruvic Acid/3NH2   36%

DHB/3NH2   233

In addition to the clay membrane cell experiments, two Hassler
Cell tests were carried out on the 3NH2/Pyruvic aldehyde
chemistry to confirm that the behaviour observed in the thin
5   films could be reproduced in a shale, Oxford clay. The
experiments consisted of confining a core of the shale in a
rubber sleeve at a pressure of 8.0 MPa while fluid was pumped
through the core at an inlet pressure of 7.5 MPa. The flow
rate, normalised to the initial rate during flow of a synthetic
10 pore fluid, is plotted for two concentrations of the pyruvic
aldehyde FIG. 1. In both Hassler cell tests the concentration
of 3NH2 was 5%.

The permeability has been reduced to 20% of the initial value,
15 measured during flow of the synthetic pore fluid. Permeability
reduction was considerably slower for the 2% pyruvic aldehyde
which levelled off at around 40% of the initial value. These
results are reasonably consistent with the clay membrane cells
with the same reactants in which the permeability of the film
20 was reduced to 60% and 10% for the low and high concentration of
the aldehyde respectively. The Hassler cell with the 5%
aldehyde shows reduction in the permeability of 6%. The
improved performance with an increase in aldehyde concentration
indicates that experiments at still higher concentration should
25 be carried out.

A wellbore simulator (SWBS) has been used to demonstrate that
the concept of the present is valid. This apparatus allows a
rock core, in which a wellbore has already been drilled, to be
30 exposed to a fluid under realistic downhole conditions. The
rock used in the experiments was Oxford Clay. Cores 8 inches in
diameter, 8 inches high and with a wellbore 1 inch in diameter
along the core axis were prepared by an initial drainage period

of 5 days at 10 MPa during which pore fluid was squeezed out of
the core. The drained core was then placed in the wellbore
simulator and its fracture pressure measured.

5   The overburden, confining and mud pressures can be controlled
independently during an experiment. Firstly, the three
pressures were stepped up to around 10 MPa while keeping any
difference between the pressures small. Next the fluid filling
the wellbore was circulated for a period of three days in the
10 cases where the rock was exposed directly to the fluid. This
was to allow for the development of any chemical interaction
between the rock and the fluid. Then the position of the
overburden piston was locked and the mud pressure was increased
in steps of 0.5 MPa while the confining pressure was maintained
15 at a constant value of 10 MPa. The mud pressure was increased
until a path opened up to allow the mud to communicate with the
confining boundary, at which point flow was observed out of the
wellbore and into the confining fluid space; usually coincident
with a pressure spike in the confining transducer. Once this
20 event occurred, the mud pressure was reduced to match the
overburden and confining once more and then all three were
reduced to ambient in step so that no further damage to the rock
took place during depressurization. At the end of a test the
rock was removed and dissected to establish the mode of failure
25 and the invasion of chemicals into the matrix.

Table 5 summarizes the results obtained for three mud systems
and two flexible lining techniques. The water based mud systems
were formulated with Xanthan gum for viscosity control and FLRXL
30 fluid loss control and three different shale stabilizers:
potassium chloride, potassium chloride + sodium silicate and
potassium chloride + sodium silicate + polyglycol. For all
three mud systems the rock fractured at pressures in a narrow
band between 15.6 and 16.5 MPa.

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Table 5. Initial wellbore simulator results

Mud	Lining	Failure MPa	Comment
KCl/Polymer	None	16.0 - 16.5	B154
Silicate	None	15.7 - 16.0	B155
Silicate + Glycol	None	15.6 - 16.0	B153
Water	Silicone Rubber	19.2 - 19.6	B157 End Effect
Water	Rubber Sleve	21.1 - 21.7	B159 O Ring Failed

The test with a silicone rubber lining was carried out as
5   follows. The core was prepared by draining at 10 MPa as
previously described, however, before it was placed in the
wellbore simulator the wellbore and the top and bottom surfaces
of the core (but not the outer boundary) were coated with a
layer of flowable silicone rubber (RS Components) to a thickness
10   of 1 to 3 mm. The rubber was allowed to cure and then the
coated core was tested to fracture with water filling the
wellbore. The lining failed at a significantly increased
pressure of between 19.2 and 19.6 MPa. The failure was caused by
an end effect as the rupture occurred where the lining passed
15   between the rock and the overburden piston and the true increase
in fracture pressure for an infinite, smooth wellbore would have
been even higher.

In the final test the core was lined with a preformed tube of
20   fluorocarbon elastomer (Adpol, UK) of 0.8 mm thickness. The

tube was sealed to the metal end platens that confine the top
and bottom of the core and then the fracturing test was carried
out as described above. With this lining the pressure limit of
one of the seals in the wellbore simulator piston failed at

5   around 21.7 MPa, at which time the lining still had not
ruptured.

The last two test clearly demonstrate the large increases in
fracture pressure possible by the application of a flexible,

10   impermeable lining to the wellbore. The pressure at which the
unsupported liners would have burst can be estimated by assuming
that they behave as an elastic hollow cylinder. The burst
pressure, P_b , is then given by

15   [2] $$P_b = \frac{r_e^2 - r_i^2}{r_e^2 + r_i^2} \sigma_t$$

where σ_t is the tensile strength of the material and r_e and r_i
are the external and internal radius of the cylinder
respectively. For the silicone rubber, which had a tensile

20   strength of 1.0 MPa, at a uniform thickness of 2 mm the burst
pressure would have been 0.2 MPa when unsupported compared to
the actual overbalance of 9.6 MPa at failure. For the preformed
elastomer tubing with a tensile strength of 15 MPa the burst
pressure would have been 1MPa when unsupported by the rock

25   compared to the maximum measured overbalance of almost 12MPa.

In FIG. 2, the main steps of the present invention are
summarized as flow chart.

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CLAIMS

1.   A method of stabilizing a wall of a wellbore penetrating a
subterranean formation, said method comprising the steps
of:
(a) introducing a layer-forming material into said wellbore
during the drilling process;
(b) letting said material form a layer supported by said
wall; and
(c) selecting said material such that the layer's shear
modulus is smaller than the formations shear modulus.

2.   The method of claim 1, using the layer to reduce the stress
concentration factor of the wall to less than zero.

3.   The method of claim 1, wherein the material forms the layer
through a chemical reaction within the wellbore

4.   The method of claim 3, wherein the material a mixture of
Pyruvic aldehyde and a triamine.

5.   The method of claim 1, wherein the material is during a
drilling operation continuously supplied from a surface
location.

6.   The method of claim 1, wherein the first reactant is a
diamine or a dihydric alcohol and the second reactant
comprises at least one carbonyl group.

7.   The method of claim 1, wherein the material is selected such
that the layer has a reduced permeability compared to the
formation permeability.

8. A method of drilling a wellbore into a potentially
    hydrocarbon bearing formation comprising the steps of
    (a) drilling part of said wellbore
    (b) introducing during said drilling steps a layer-forming
5   material into said wellbore;
    (c) letting said material form a layer supported by said
    wall; and
    (d) selecting said material such that the layer's shear
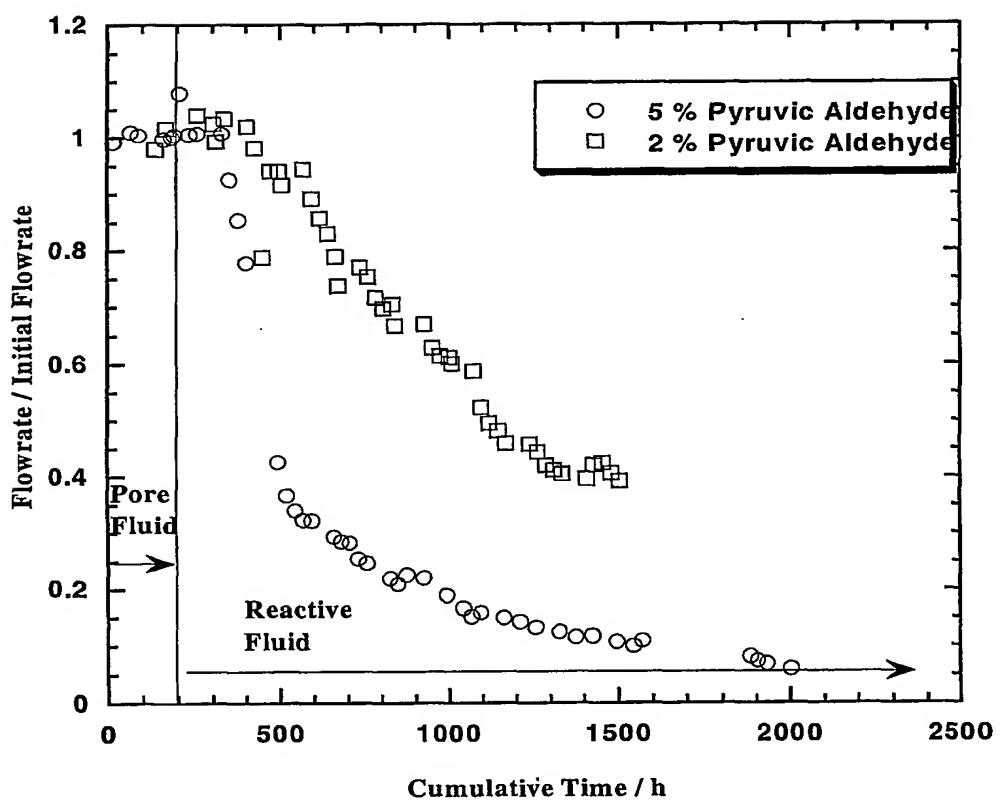   modulus is smaller than the formations shear modulus.
10

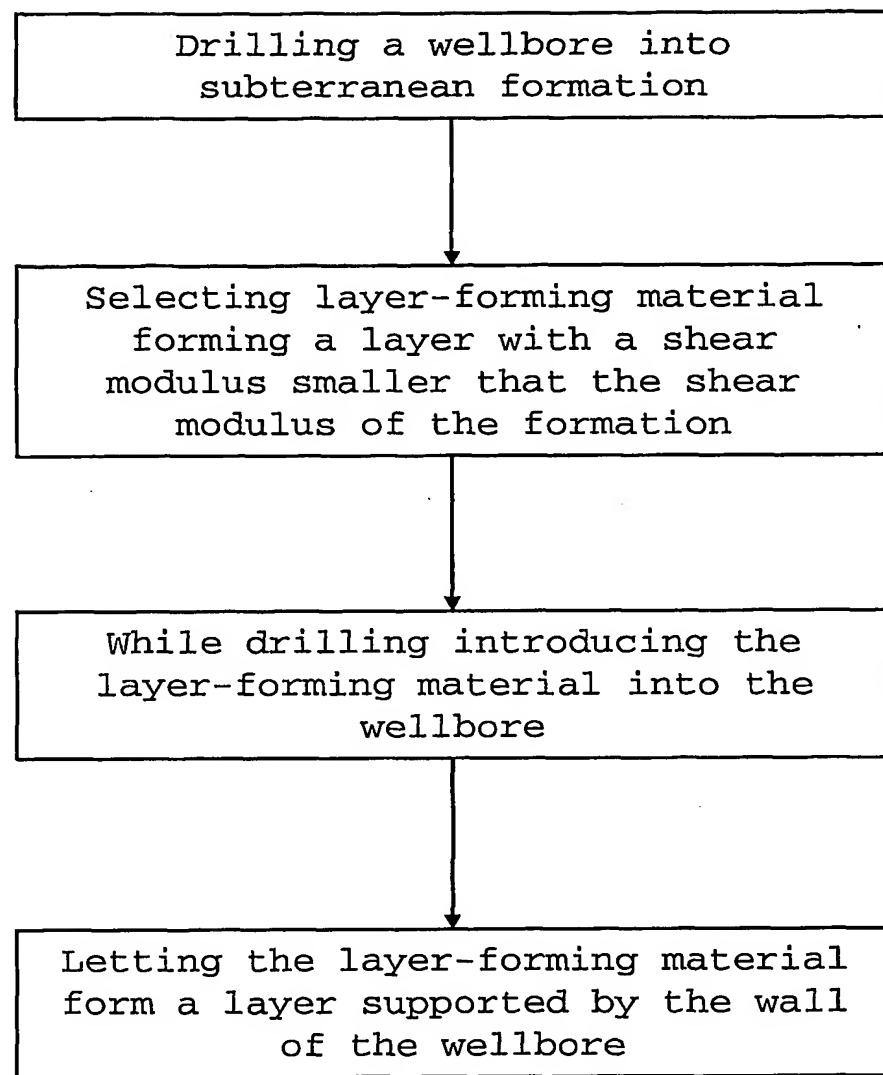FIG. 1

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┌─────────────────────────────────────┐
│      Drilling a wellbore into        │
│      subterranean formation          │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│   Selecting layer-forming material   │
│    forming a layer with a shear      │
│   modulus smaller that the shear     │
│     modulus of the formation         │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│   While drilling introducing the     │
│    layer-forming material into the   │
│              wellbore                │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│  Letting the layer-forming material  │
│  form a layer supported by the wall  │
│          of the wellbore             │
└─────────────────────────────────────┘
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FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   E21B33/138

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7   E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 784 223 A (WORRALL ROBERT N ET AL) 15 November 1988 (1988-11-15) column 2, line 16 – line 28 ---	1-8
A	US 5 911 282 A (CHATTERJI JITEN ET AL) 15 June 1999 (1999-06-15) cited in the application column 3, line 47 – line 67 ---	1-8
A	WO 99 31353 A (SOFITECH NV ;SCHLUMBERGER CANADA LIMITED (CA); SCHLUMBERGER CIE DOW) 24 June 1999 (1999-06-24) cited in the application page 3, line 25 –page 4, line 14 ---	1-8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2001	04/09/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Garrido Garcia, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 766 984 A (NIMERICK K) 23 October 1973 (1973-10-23) column 2, line 14 – line 22 column 7, line 46 – line 55 ---	1-8
A	RU 2 032 067 C (VSESOYUZNYJ NI I PI KREPLENIYU) 27 March 1995 (1995-03-27) abstract -----	1

INTERNATIONAL SEARCH REPORT

formation on patent family members

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US 5911282	A	15-06-1999	US	5873413 A	23-02-1999
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